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(11) EP 0 331 424 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
17.04.1996 Bulletin 1996/16

(51) Int. Cl.⁶: C04B 35/58

(21) Application number: 89301965.3

(22) Date of filing: 28.02.1989

(54) Molded articles formed of silicon nitride based ceramic and process for producing same
Formkörper aus Keramik auf Siliciumnitrid-Basis und Verfahren zu ihrer Herstellung
Articles façonnés en céramique à base de nitrure de silicium et procédé de leur fabrication

(84) Designated Contracting States:
BE DE FR GB IT SE

(30) Priority: 29.02.1988 JP 46966/88
29.02.1988 JP 46967/88
03.03.1988 JP 48713/88

(43) Date of publication of application:
06.09.1989 Bulletin 1989/36

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(56) References cited:
EP-A- 0 175 382 EP-A- 0 227 283
EP-A- 0 250 073 FR-A- 2 197 829
FR-A- 2 599 745 US-A- 4 659 850

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Description

This invention relates to a shaped body formed of a silicon nitride-based ceramic and to processes for producing same.

Silicon nitride has been attracting much attention for its favorable properties such as resistance to heat, oxidation, wearing, chemicals and impact and electrical insulation. It will find wide use for gas turbine blades, engine parts, cutting tools, etc. in the near future.

The following molded or otherwise shaped, ceramic articles have thus far been proposed:

1) Molded articles formed of a homogeneous mixture of silicon carbide and silicon nitride obtained by calcining an organosilazane which is produced by reaction of a halogenosilane with ammonia (Japanese Tokkyo Kokai Nos. 49-69717, 49-20206 and 62-202863 and United States patent No. 4,482,669);

2) Coating films, plates and crucibles formed of a silicon nitride obtained by the CVD method from silicon tetrachloride and ammonia (FC Report 5, No. 8, 287 (1987));

3) Molded articles obtained a method including the steps of filling a mold cavity with a liquid silazane obtained by reacting a dihydrosilazane with ammonia, and thermally decomposing the silazane at 500-1200 °C in an oxygen-free and moisture-free atmosphere (United States patent No. 4,397,828, Material Science Research Vol. 17, 271 (1984), Comm. Amer. Ceram. Soc., C-13 (1983));

4) Continuous inorganic fibers consisting essentially of Si, N and O and obtained by a method including the steps of infusibilizing polycarbosilane fibers having a Si-C skeleton with an oxidizing gas, and nitrifying the infusible product at 800-1650 °C in the atmosphere of ammonia (Japanese Tokkyo Kokai No. 61-12915);

5) Silicon nitride powder of alpha-type crystals obtained by a method including the steps of nitrifying a polysilazane containing a recurring unit of =Si-NH- at 350-1000 °C in the atmosphere of ammonia, and calcining the nitrification product at 1300-1700 °C (Japanese Tokkyo Kokai No. 61-151005); and

6) Ceramic materials obtained by a method including the steps of treating a polysilazane with steam or a mixture of steam and oxygen to render the polysilazane infusible, and calcining the treated product at 750 °C or more under vacuum or in the atmosphere of an inert gas or ammonia (Japanese Tokkyo Kokai No. 61-295273).

These shaped ceramic bodies are, however, not fully satisfactory for commercial applications for the reasons as set forth below:

The molded article of (1) above has a high content of free carbon because its raw material contains a high content of carbon atoms. The residual carbon at a high

temperature causes a phase separation or reacts so that the inherent properties of ceramics such as electrical insulation, resistance to impact and mechanical strength are reduced. The molded article of (2) is economically disadvantageous because its manufacturing process is complicated and requires much costs. Since the method for the production of the article of (3) fails to sufficiently form cross-linkages before the thermal decomposition at 500-1200 °C, low boiling point silazanes and radicals are apt to evolved and vaporized during the thermal decomposition so that the formation of cracks or voids are facilitated during the course of the thermal decomposition and, thus, the molded articles have diameters of only several mm and are fragile. It is not possible to obtain shaped bodies other than fibers in the case of (4) because, during the nitrification stage, reactions resulting in the cleavage of Si-CH₃ bonds and Si-CH-Si bonds proceed violently, thereby to form cracks and voids. In the case of (5), the formation of cross-linkages are not effected sufficiently before the nitrification at 350-1600 °C, low boiling point silazanes and radicals are apt to evolved and vaporized during the thermal decomposition so that the formation of cracks or voids are facilitated during the nitrification treatment and, thus articles having desired shapes cannot be obtained. In the case of (6), the infusibilization treatment causes Si-H bonds of the polysilazane to be hydrolysed violently so that articles having a desired shape cannot be obtained.

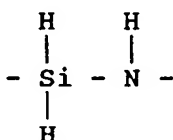
For the purpose of improving mechanical strength, it is known to incorporate a reinforcing material into shaped ceramic articles. In known composite molded articles, ceramic powder such as of silicon nitride, silicon carbide, alumina or silica is used for the formation of the ceramic matrices. The use of such ceramic powder for the formation of ceramic matrix of the composite article, however, causes a difficulty in uniformly dispersing the reinforcing material therinto. As a result, the hoped for improvement in mechanical strengths such as breaking strength and toughness cannot be attained in a satisfactory manner.

Molded articles of a ceramic material produced by sintering ceramic powder are also known. Since it is difficult to sinter ceramic powder such as of silicon nitride or silicon carbide, a sintering aid (or binder) is generally used for densifying the molded articles. For example, alumina, yttria or magnesia is used for the formation of molded articles of silicon nitride ceramic. Also known is a preceramic polymer such as a polycarbosilane, a polytitanocarbosilane or a polymethylsilazane as such a sintering aid. The former, inorganic binder should form a glass phase in order for the ceramic powder to be sintered at a low temperature. The formation of the glass phase, however, unavoidably causes a reduction of resistance to oxidation, heat and chemicals. The latter, organic binder cannot sufficiently increase the density and strength of the molded articles because of its low thermal decomposition yield.

The present invention has been made in view of the foregoing problems in the art of ceramic shaped articles.

In accordance with the present invention there is provided a shaped body containing a silicon nitride-based ceramic containing Si and N in amounts providing an atomic ratio N/Si of 0.04 to 3, and at least one metal selected from Groups IIA, III, IV and V of the Periodic Table, in amount providing the following atomic ratio:

M/Si : 9 or less, where M stands for said metal or metals of Groups IIA, III, IV and V, and optionally oxygen in amount providing an atomic ratio O/Si of 0.05-15, wherein said ceramic is obtained from a polymetallosilazane having a metal/silicon atomic ratio of 0.001-30 and a number molecular weight of 200-500,000 and obtained by reacting a raw material having a molecular weight of 100-50,000 and the following recurring unit:



with a metal alkoxide of the formula $\text{M}(\text{OR})_n$ wherein M is a metal of Group IIA, III, IV or V of the Periodic Table, R_4 is hydrogen, an alkyl group having 1-20 carbon atoms or an aryl group and n is the valence of the metal M, with the proviso that at least one R_4 substituent is alkyl or aryl; and wherein the carbon content of the ceramic is such that the C/Si atomic ratio is 0.66 or less.

The present invention will now be described in detail below.

The novel molded body according to the present invention is formed of a silicon nitride-based ceramic containing Si and N in amounts providing an atomic ratio N/Si of 0.04 to 3.

The silicon nitride-based molded body also contains at least one metal of Groups IIA, III, IV and V of the Periodic Table, in amounts providing the following atomic ratio:

M/Si : 9 or less, where M stands for the metal or metals.

The silicon nitride-based molded body may optionally also contain oxygen. If present, the O/Si atomic ratio should be within the range 0.05-15.

Atomic ratios outside of the above ranges tend to cause a reduction of the mechanical strength, resistance to heat and wear or the like properties of the molded body. The incorporation of oxygen can improve wettability of the molded body. Incorporation of a metal from the defined groups into the ceramic provides unique properties which vary with the kind of the metal used. Generally, electrical conductivity, dielectric property and compatibility with a reinforcing material such as fibers can be improved by the addition of the metal. Preferred atomic

ratios are as follows:

N/Si	0.1 to 1.7,
O/Si	0.1 to 10, and
M/Si	5 or less.

More preferred ranges are as follows:

N/Si	0.3 to 1.3,
O/Si	0.3 to 4,
M/Si	2.5 or less.

The metals M are those of the groups IIA, IIIA, IIIB, IVA, IVB, Va and Vb of the Periodic Table. Illustrative of suitable metals are Be, Mg, Ca, Sr, Ba, Sc, Y, lanthanoid elements, actinoid elements, B, Al, Ga, In, Tl, Ti, Zr, Hf, Si, Ge, Sn, Pb, V, Nb, Ta, As, Sb and Bi. Above all, Al, Ti and Zr are especially preferred.

In the silicon nitride based ceramic of the present invention the C/Si atomic ratio must not exceed 0.66.

The ceramic may contain fine ceramic crystallites having a diameter of 10 μm or less or may be substantially amorphous. Formation of crystallites having too large a diameter is disadvantageous because of reduction of mechanical strength. Preferred diameter of the ceramic crystallites is 2,000 \AA or less, more preferably 1,000 \AA or less. The size of the ceramic crystallites is measured by the Jones method from an X-ray diffraction half value width. It is also preferred that the ceramic molded body have a three-point bending strength of 20 Kg/cm^2 or more, preferably 100 Kg/cm^2 or more, for reasons of its satisfactory mechanical strength. The three-point bending strength is measured with a universal testing machine under the following conditions:

cross sectional area of sample	4-7 mm^2
span	10 mm
loading speed	1 mm/minute

The shaped body according to the present invention may be produced, for example, by solidifying a polymetallosilazane or its derivative under vacuum or in the atmosphere of an inert gas, a reducing gas, an oxidizing gas or a mixture thereof, followed by calcination in such an atmosphere.

The shaped body according to the present invention includes (a) one which is obtained from the above-defined polymetallosilazane only, (b) one which is

obtained from the above polymetallosilazane and a small amount of reinforcing powder (in this case, the polymetallosilazane gives a ceramic matrix in which the reinforcing powder is dispersed), (c) one which is obtained from the above polymetallosilazane and reinforcing fibers (in this case, too, the polymetallosilazane forms a ceramic matrix in which the reinforcing fibers are dispersed), (d) one which is obtained from the above polymetallosilazane and a relatively large amount of ceramic powder (in this case, the polymetallosilazane serves to act as a binder). Methods of producing shaped bodies of these types will be described in detail below.

Shaped bodies of (a) and (b) types may be produced by the same method which includes solidifying a raw material containing the above polymetallosilazane in a mold cavity and calcining the solidified mass. The raw material may further contain a reinforcing powder such as ceramic powder and/or a hardener. Examples of such ceramic powder include metal nitrides, metal carbides and metal oxides. The use of the ceramic powder can prevent the occurrence of cracks during succeeding calcination and can improve mechanical strengths of the molded body. The hardener may be, for example, an organic amine such as an alkyl amine or an alkyldiamine; an acid anhydride such as oxalic anhydride or malonic anhydride; an isocyanate such as methyl isocyanate or dimethylsilyldiisocyanate; a thiol such as butane dithiol or benzene dithiol, an imide such as malonimide or succinimide; a metal alkoxide such as of an element of the group IIa, III, IV or V of the Periodic Table; or an inorganic halide such as of iron, cobalt, nickel, copper, silver, gold, mercury, zinc, ruthenium, palladium, indium, titanium, hafnium, zirconium, aluminum, boron or phosphorus. The amount of the reinforcing powder is generally 0.1-60 %, preferably 10-40 % based on the total weight of the ceramic matrix and the powder.

The raw material is placed into a mold cavity and is solidified and simultaneously molded. The solidification conditions involving temperature, pressure, environmental atmosphere and period of time may vary according to the kind of the polysilazane used and amount and kind of the hardener or reinforcing powder.

When a solid polymetallosilazane is used, it is first dissolved in an organic solvent such as a hydrocarbon, a halogenated hydrocarbon or an ether. The solution is then poured into the mold cavity and is heated under a reduced pressure or ambient pressure to remove the organic solvent, thereby to obtain a solidified and molded product.

When the polymetallosilazane to be used is a liquid, it is filled in a mold cavity and gradually heated from room temperature to about 400 °C at a pressure up to about 10 atm. for a period of time of about 0.5-72 hours in the atmosphere of an inert gas such as nitrogen or argon; a reducing gas such as ammonia, methamine or hydrazine; an oxidizing gas such as air, oxygen or ozone; or a mixed gas of the above. If desired, the solid polysilazane as such may be filled in the mold cavity and heated grad-

ually to about 400 °C at a pressure of up to 10 atm. in a suitable atmosphere as exemplified above.

The solidification is considered to proceed in the following mechanisms. Under a reducing or oxidizing gas atmosphere, the polymetallosilazane is considered to undergo cross-linking reaction as a result of substitution of hydrogen of its Si-H groups. For instance, in the case of NH₃, there are formed Si-NH-Si cross-linkages and in the case of O₂, Si-O-Si cross-linkages are formed, so that the polymetallosilazane becomes solid. When the solidification is performed in an inert gas atmosphere or under vacuo, cross-linking reactions are considered to occur as a result of intermolecular or intramolecular dehydrogenative condensation.

Any known mold can be used for the above solidification. It is advisable to coat the inside of the mold cavity with a mold releasing agent such as a silicone-based agent or a grease with or without dilution with an organic solvent.

The thus formed solidified product is then gradually heated to 500-1700 °C, preferably 800-1300 °C at a heating rate of 20 °C/min or less, preferably 5 °C/min or less and maintained at that temperature for 48 hours or less, thereby to effect calcination and to obtain a desired molded body. A calcination temperature exceeding 1700 °C is not desirable because of a possible occurrence of decomposition. Too low a calcination temperature below 500 °C is also disadvantageous because of insufficient formation of ceramic and insufficient increase of mechanical strengths. The thus obtained ceramic molded body may be impregnated with the above polymetallosilazane, followed by solidification and calcination, so that the surface portion of the molded body becomes more dense.

A shaped body of the above type (c), which is a fiber-reinforced composite shaped body, may be produced by impregnating fibers with the above-described polymetallosilazane and removing the solvent to form a prepreg (fiber-reinforced preceramic polymer). If desired, the impregnation may be followed by a treatment for solidifying the polymetallosilazane. The prepreg is then cut into a desired pattern and cut patterns are superimposed and laminated, followed by calcination and press molding to give a molded, composite body. The solidification may be performed under a reduced pressure or in the atmosphere of an inert gas, an oxidizing gas, a reducing gas or a mixed gas thereof. Ceramic powder and/or hardener, which are described previously, may be also used in conjunction with the polysilazane for impregnation into the fibers. The hardener can facilitate the solidification of the polymetallosilazane while the ceramic powder can prevent the occurrence of cracking of the molded body and can improve the mechanical strengths of the molded body. The solidification of the polymetallosilazane with which the fiber have been impregnated can be performed under the same conditions as those described above in connection with the production of the molded body of a type (a) or (b).

The fibers to be used as a reinforcing material may be, for example, glass fibers, carbon fibers, silicon nitride fibers, boron fibers, silicon carbide fibers, alumina fibers, asbestos fibers, silica fibers, silica-alumina fibers, boron nitride fibers, boron carbide fibers, silicon nitride-titanium carbide fibers, titanium boride fibers, silicon-titanium-carbon-oxygen fibers, silicon-zirconium-carbon-oxygen fibers, silicon-metal-nitrogen-oxygen-carbon fibers where said metal is at least one selected from those of the group IIa, III and V of the Periodic Table or tungsten fibers. The fibers may be continuous, chopped or in the form of fabrics. Preferably, the reinforcing fibers are silicon nitride-based ceramic fibers containing Si and N in amounts providing the atomic ratio N/Si of 0.3 to 3 and exhibiting an X-ray small angle scattering such that the ratio of the intensity of the small angle scattering of the fibers to that of air is 1 to 20 at scattering angles 0.5° and 1°. The silicon nitride-based ceramic fibers may further contain at least one element selected from O, C, H and metals (those of groups IIa, III, IV and V of the Periodic Table) in amounts providing the following atomic ratios:

O/Si	15 or less,
C/Si	7 or less,
H/Si	15 or less,
M/Si	5 or less, where M stands for the metals.

The ceramic fibers may either be amorphous when heated at a temperature of 1200 °C for one hour in the atmosphere of an inert gas or contain fine ceramic crystallites having a diameter of 10 µm or less. The reinforcing fibers are used in an amount of 5-75 %, preferably 20-60 % by volume based on the total volume of the fiber-reinforced ceramic molded body.

The thus obtained prepreg is, preferably after the solidification, then calcined and sintered in the atmosphere of an inert gas, a reducing gas, an oxidizing gas or a mixed gas thereof. A hot press method, an HIP method or slip cast method may be suitably adopted. The calcination and sintering may be performed at temperatures of 700-2500 °C, preferably 1000-2000 °C, more preferably 1100-1800 °C at a pressure of from ambient pressure to 2000 Kg/cm² for a period of time of 48 hours or less with a heating rate of 20 °C/min or less preferably 5 °C/min or less. The fiber-reinforced ceramic shaped body can also be obtained by any customarily employed shaping method such as a hand lay up method, vacuum pack method, press pack method, autoclave method, spray up method, cold press method, continuous laminating method, matched die method, preform press method, mat press method, prepreg cross press method, filament winding method, sheer molding compound method, bulk molding compound method, stamping method, transfer method, injection method, centrifuging method, rolling method, rolling laminating method or mold-pouring method.

The calcined and/or sintered composite ceramic shaped body may be impregnated with the above polymetallosilazane, followed by solidification and calcination. By repeating such operations it is possible to obtain a molded body having more dense surface.

The shaped article of the type (d) above in which the polymetallosilazane serves to act as a binder for ceramic powder may be obtained by forming a slurry containing the polymetallosilazane and the ceramic powder in a suitable solvent and subjecting the slurry to a slurry molding. Alternatively, the slurry thus formed is into granules by evaporation of the solvent to dryness such as by means of a spray dryer and the resulting is subjected to a press molding. The polymetallosilazane, in this case, serves as a binder not only in the press molding stage but also in the granule forming stage.

As the solvent for forming the slurry, there may be used an aliphatic hydrocarbon, a halogenated hydrocarbon, or aliphatic or alicyclic ether. Illustrative of suitable solvents are methylene chloride, chloroform, carbon tetrachloride, bromoform, ethylene chloride, ethylidene chloride, trichloroethane, tetrachloroethane, ethyl ether, isobutyl ether, ethyl butyl ether, butyl ether, 1,2-dioxethane, dioxane, dimethyldioxane, tetrahydrofuran, tetrahydropyran, pentane, hexane, isohexane, methylpentane, heptane, isoheptane, octane, isooctane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, benzene, toluene, xylene and ethylbenzene.

Any ceramic powder including metal nitrides, metal carbides and metal oxides may be used for the purpose of the present invention. The powder is generally used in an amount of 40-99.9 %, preferably 50-90 % based on the total weight of the polysilazane binder (on the calcined basis) and the powder. If desired, the calcined and/or sintered ceramic molded body may be impregnated with a solution of a polymetallosilazane, followed by solidification and calcination. By repeating such operations it is possible to obtain a dense shaped body.

The shaped product thus obtained by the slurry molding or the press molding is then calcined and sintered to obtain a molded body according to the present invention in which the interstices between the ceramic powder are filled with amorphous or fine crystallites of silicon nitride formed as a result of the decomposition of the polysilazane. The calcination and sintering can be performed under vacuum or in the atmosphere of an inert gas, a reducing gas, an oxidizing gas or a mixed gas thereof at a temperature of 600-2300 °C.

The following examples will further illustrate the present invention.

Reference Example 1

Preparation of Perhydropolysilazane:

To a four-necked 10 liter flask equipped with a gas feed conduit, a mechanical stirrer and a Dewar condenser, an oxygen-free, dry nitrogen gas was fed to

replace the air within the flask therewith. After charging 4900 ml of dry pyridine (deaerated), the flask was cooled in an ice bath. Then 744 g of dichlorosilane were added into the flask to form a white precipitate of adduct ($\text{SiH}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$). Subsequently, with stirring and cooling in the ice bath, 735 g of ammonia which had been passed successively through a sodium hydroxide-containing tube and an active carbon-containing tube was bubbled through the reaction mixture within the flask. The reaction was completed by heating the contents in the flask at 100 °C. After completion of the reaction, the reaction mixture was centrifuged and the supernatant was washed with dry pyridine, followed by filtration in a nitrogen atmosphere to give 5100 ml of a filtrate containing perhydropolysilazane. The polysilazane was found to have a number-average molecular weight of 980.

Reference Example 2

Preparation of Polyaluminosilazane:

To a four-necked 2 liter flask equipped with a gas feed conduit, a magnetic stirrer, a seal cap and a Dewar condenser, a dry argon gas was fed to replace the air within the flask therewith. After charging 14.7 g (72 mmol) of aluminum triisopropoxide, a 5 weight % solution of perhydropolysilazane in a dry o-xylene (the perhydropolysilazane was similar to that obtained in Reference Example 1) was fed to the flask using a syringe with stirring to obtain a homogeneous solution. The solution was then reacted at 80 °C with stirring in the atmosphere of argon. As a result, the colorless solution became light yellow. Gel permeation chromatography using a polystyrene as a standard revealed the formation of polyaluminosilazane having a number-average molecular weight of 1750 and a weight-average molecular weight of 14500.

Reference Example 3

Preparation of Polytitanosilazane:

To a four-necked, 2 liter flask equipped with a gas feed conduit, a magnetic stirrer, a seal cap and a Dewar condenser, a dry nitrogen gas was fed to replace the air within the flask therewith. After charging 1000 g of a 5 weight % solution of perhydropolysilazane in a dry o-xylene (the perhydropolysilazane was similar to that obtained in Reference Example 1) to the flask, a solution (6.5 ml) of titanium tetraisopropoxide (7.0 g, 24.6 mmol) in dry xylene was fed to the flask using a syringe with stirring. The reaction solution was changed from colorless to light brown, purple and finally black as the reaction proceeded. After completion of the reaction, the solvent was removed by distillation in vacuo to obtain, as a dark brown solid, polyhydrotitanosilazane with a yield of 84.0 %. Gel permeation chromatography using a polystyrene as a standard revealed that the product had a number-

average molecular weight of 1800 and a weight-average molecular weight of 15000.

Example 1

The polyaluminosilazane obtained in Reference Example 2 and containing a small amount of a solvent was poured into a glass mold whose inside surface was lined with a mold release agent. The mold containing the polyaluminosilazane was then placed in an autoclave and the solvent was removed by evaporation to dryness by maintaining the autoclave in vacuum. Thereafter, nitrogen gas was introduced to the autoclave to a pressure of 3 atm. and the mold was heated to 80°C at that pressure, so that a white, translucent bar (2.5 mm x 3 mm x 20 mm) was obtained. The bar was then heated to 800°C at a heating rate of 0.1°C/min in the atmosphere of nitrogen to form a ceramic bar. Chemical and X-ray diffraction analyses revealed that the ceramic bar consisted of Al, Si, N, O and C, was amorphous and had an N/Si atomic ratio of 1.02, an O/Si atomic ratio of 0.37, an Al/Si atomic ratio of 0.09 and a C/Si atomic ratio of 0.66. The three point bending strength of the plate was 105 Kg/cm².

Example 2

Using the polytitanosilazane obtained in Reference Example 3 in lieu of the polyaluminosilazane Example 1 was repeated in the same manner as described. The ceramic bar thus obtained was found to have atomic ratios N/Si of 0.96, O/Si of 0.24, Ti/Si of 0.02 and C/Si of 0.32, to be amorphous and to have a bending strength of 93 Kg/cm².

Example 3

A bundle of silicon nitride fibers (500 filaments) was wound around a straight-sided bobbin and the bobbin was placed in a mold cavity, into which a 75 wt % o-xylene solution of the polyaluminosilazane obtained in Reference Example 2 was poured to impregnate the fibers therewith. The wound bundle was then pressed at a pressure of 100 Kg/cm², placed in an autoclave molding machine and molded at 130 °C under a nitrogen pressure of 5 Kg/cm², thereby to obtain a flat plate. This was cut into prepreg plates having a size of 15 mm x 50 mm and a width of 1 mm. The prepreg plates were heated to 1000 °C for calcination in the atmosphere of nitrogen. The calcined plates were laminated and subjected to hot press at a temperature of 1700 °C and a pressure of 400 Kg/cm², to obtain a fiber-reinforced, composite, molded body having a fiber content of 40 volume %. The molded body was found to have a deflective strength of 57 Kg/mm² at 1400 °C (when subjected to a stress applied in the direction perpendicular to the axis of the fiber) and a 1.5 times as high fracture toughness K_{IC} as that of a molded body formed only of the matrix ceramic. The

matrix of the fiber-reinforced body had atomic ratios N/Si of 1.00, O/Si of 0.36, C/Si of 0.64 and Al/Si of 0.09.

Example 4

Using a 80 % solution o-xylene solution of the perhydrotitanopolysilazane obtained in Reference Example 3 in place of the perhydroaluminopolysilazane solution, Example 3 was repeated in the same manner as described, thereby to obtain a fiber-reinforced, composite, molded body having a fiber content of 40 volume %. The molded body was found to have a deflative strength of 55 Kg/mm² at 1400 °C (when subjected to a stress applied in the direction perpendicular to the axis of the fiber) and a 1.8 times as high fracture toughness K_{IC} as that of a molded body formed only of the matrix ceramic. The matrix of the fiber-reinforced body had atomic ratios N/Si of 0.95, O/Si of 0.23, C/Si of 0.30 and Ti/Si of 0.02.

Example 5

A suitable amount of o-xylene, 90 parts by weight of an equimolar mixture of Si₃N₄ powder having an average particle size of 1 μm, Al₂O₃ powder having an average particle size of 0.3 μm and AlN powder having an average particle size of 0.5 μm, and 10 parts by weight of powder of the polyaluminosilazane obtained in Reference Example 2 were mixed with each other and the mixture was dried, ground to a powder and rated to have a particle size of 100 mesh or finer. The resulting powder was press-molded at a pressure of 2000 Kg/cm² to obtain a molded product of 10 mm x 50 mm x 5 mm. The molded product was then heated to 1550 °C at a heating rate of 200 °C/hour in a nitrogen gas atmosphere for calcination, thereby to obtain a molded body having a bulk density of 2.90 g/cm³ and a deflative strength of 35.8 Kg/mm².

Comparative Example 1

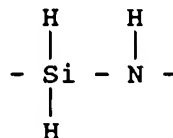
Example 5 was repeated in the same manner as described except that no polyaluminosilazane was used. The molded product was found to have a bulk density of 2.2 g/cm³.

Claims

1. A shaped body containing a silicon nitride-based ceramic containing Si and N in amounts providing an atomic ratio N/Si of 0.04 to 3, and at least one metal selected from Groups IIA, III, IV and V of the Periodic Table in amount providing the following atomic ratio:

M/Si : 9 or less, where M stands for said metal or metals of Groups IIA, III, IV and V, and optionally oxygen in amount providing an atomic ratio O/Si of 0.05-15, wherein said ceramic is obtained from a polymetallosilazane having a metal/silicon atomic ratio of

0.001-30 and a number molecular weight of 200-500,000 and obtained by reacting a raw material having a molecular weight of 100-50,000 and the following recurring unit:



with a metal alkoxide of the formula M(OR₄)_n wherein M is a metal of Group IIA, III, IV or V of the Periodic Table, R₄ is hydrogen, an alkyl group having 1-20 carbon atoms or an aryl group and n is the valence of the metal M, with the proviso that at least one R₄ substituent is alkyl or aryl; and wherein the carbon content of the ceramic is such that the C/Si atomic ratio is 0.66 or less.

2. A shaped body as set forth in Claim 1, wherein said atomic ratios are as follows:

N/Si:	0.1-1.7, and
M/Si:	5 or less, and optionally
O/Si:	0.1-10.

3. A shaped body as set forth in Claim 2, wherein said atomic ratios are as follows:

N/Si:	0.3-1.3, and
M/Si:	2.5 or less, and optionally
O/Si:	0.3-4.

4. A shaped body as set forth in any preceding claim, and having a three-point bending strength of 20 Kg/cm² or more.
5. A shaped body as set forth in any preceding claim, wherein said ceramic contains fine ceramic crystallites having a diameter of 2000 Å or less.
6. A shaped body as set forth in any one of Claims 1-4, wherein said ceramic is substantially amorphous in nature.

7. A shaped body as set forth in any preceding claim, further containing a reinforcing material.

8. A shaped body as set forth in Claim 7, wherein said reinforcing material is in the form of powder and is homogeneously dispersed in said molded body with said ceramic serving as a matrix.

9. A shaped body as set forth in Claim 8, wherein said powder is used in an amount of 0.1-60% based on the total weight of said ceramic matrix and said powder.

10. A shaped body as set forth in Claim 8 or Claim 9, wherein said reinforcing material is ceramic powder.

11. A shaped body as set forth in Claim 7, wherein said reinforcing material is in the form of powder bound with said ceramic serving as a binder.

12. A shaped body as set forth in Claim 11, wherein said powder is used in an amount of 40-99.9% based on the total weight of said ceramic binder and said powder.

13. A shaped body as set forth in Claim 7, wherein said reinforcing material is in the form of fibers dispersed in said shaped body with said ceramic serving as a matrix.

14. A shaped body as set forth in Claim 13, wherein said fibers are used in an amount of 5-75% by volume.

15. A shaped body as set forth in Claim 7, wherein said reinforcing material is a mixture of fibers and powder, said fibers being dispersed in said shaped body with said ceramic serving as a matrix, and said powder being dispersed in said ceramic matrix.

16. A shaped body as set forth in Claim 15, wherein said fibers are used in an amount of 5-75% by volume.

17. A shaped body as set forth in Claim 15 or Claim 16, wherein said powder is used in an amount of 0.1-60% based on the total weight of said ceramic matrix and said powder.

18. A process for producing a shaped body as defined in any preceding claim, comprising the steps of:
filling a mold cavity with a raw material containing said polysilazane;

heating said raw material at a temperature from room temperature to about 400°C to solidify said polysilazane in said mold cavity; and

calcining said solidified product to obtain a molded article formed of said silicon nitride-based ceramic, by heating said solidified product to 500°-1700°C at a heating rate of 20°C/min or less.

19. A process as set forth in Claim 18, wherein said raw material further contains a ceramic powder so that said ceramic powder is dispersed in a matrix of said silicon nitride-based ceramic.

20. A process as set forth in Claim 19, wherein said ceramic powder is formed of a metal nitride, a metal carbide or a metal oxide.

21. A process for producing a shaped body as defined in any one of Claims 1-7, comprising the steps of:
impregnating the fibers with a liquid containing said polysilazane;
solidifying said polysilazane to form a prepreg; and
calcining and sintering the thus formed prepreg at a temperature of 700°-2500°C with a heating rate of 20°C/min or less, to form a fiber-reinforced silicon nitride-based ceramic body.

22. A process as set forth in Claim 21, wherein said liquid further contains finely divided ceramic powder dispersed therein.

23. A process for producing a shaped body as defined in any one of Claims 1-17, comprising the steps of:
providing a solution of said polysilazane;
mixing said solution with a finely divided ceramic powder to form a slurry;
molding said slurry to form a molded body with said polysilazane serving as a binder; and
calcining said molded body at a temperature of 600°-2300°C to form a molded silicon nitride-based ceramic article.

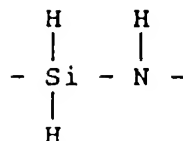
Patentansprüche

1. Formteil aus Keramikmaterial auf Siliciumnitridbasis, das Si und N in Mengen, die ein Atomverhältnis N/Si von 0,04 - 3 ergeben, und wenigstens ein aus den Gruppen IIA, III, IV und V des Periodensystems ausgewähltes Metall in einer Menge, die das folgende Atomverhältnis ergibt:

M/Si : 9 oder kleiner,

worin M für das Metall oder die Metalle der Gruppen IIA, III, IV und V steht, sowie wahlweise Sauerstoff in einer Menge enthält, die ein Atomverhältnis O/Si von 0,05 - 15 ergibt, dadurch gekennzeichnet, daß das Keramikmaterial aus Polymetallosilazan mit einem Metall-/Silicium-Atomverhältnis von 0,001 - 30 und einer relativen Molekülmasse von 200 - 500 000 und dadurch erhalten wird, daß ein Ausgangsmaterial mit einer relativen Molekülmasse von 100 - 50 000 und der folgenden sich wiederholenden Ein-

heit:



mit einem Metallalkoxid der Formel $\text{M}(\text{OR}^4)_n$ zur Reaktion gebracht wird, worin M ein Metall der Gruppe IIA, III, IV oder V des Periodensystems darstellt, R_4 Wasserstoff, eine Alkylgruppe mit 1 - 20 Kohlenstoffatomen oder eine Arylgruppe ist und n die Wertigkeit des Metalls M angibt unter der Voraussetzung, daß wenigstens ein R_4 -Substituent Alkyl oder Aryl ist; und dadurch gekennzeichnet, daß der Kohlenstoffgehalt des Keramikmaterials so gewählt ist, daß das Atomverhältnis N/Si bei 0,66 oder darunter liegt.

2. Formteil gemäß Anspruch 1, dadurch gekennzeichnet, daß folgende Atomverhältnisse vorliegen:

N/Si:	0,1 - 1,7 und
M/Si:	5 oder kleiner sowie wahlweise
O/Si:	0,1 - 10

3. Formte gemäß Anspruch 1, dadurch gekennzeichnet, daß folgende Atomverhältnisse vorliegen:

N/Si:	0,3 - 1,3 und
M/Si:	2,5 oder kleiner sowie wahlweise
O/Si:	0,3 - 4

4. Formte gemäß einem der vorhergehenden Ansprüche mit einer Dreipunktiegefestigkeit von 20 kg/cm² oder mehr.
5. Formte gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Keramikmaterial feine Keramikkrystallite mit einem Durchmesser von 2 000 Å oder weniger enthält.
6. Formteil gemäß einem der Ansprüche 1 - 4, dadurch gekennzeichnet, daß das Keramikmaterial in seiner Beschaffenheit im wesentlichen amorph ist.

7. Formte gemäß einem der vorhergehenden Ansprüche des weiteren mit einem Verstärkungsmaterial.
8. Formte gemäß Anspruch 7, dadurch gekennzeichnet, daß das Verstärkungsmaterial ein Pulver und in dem Formteil homogen dispergiert ist, wobei das Keramikmaterial als Grundmasse dient.
9. Formteil gemäß Anspruch 8, dadurch gekennzeichnet, daß das Pulver in einer Menge von 0,1 - 60 %, bezogen auf die Gesamtmasse der Keramikgrundmasse und des Pulvers, verwendet wird.
10. Formteil gemäß Anspruch 8 oder 9, dadurch gekennzeichnet, daß das Verstärkungsmaterial ein Keramikpulver ist.
11. Formteil gemäß Anspruch 7, dadurch gekennzeichnet, daß das Verstärkungsmaterial ein mit dem als Bindemittel dienenden Keramikmaterial gebundenes Pulver ist.
12. Formte gemäß Anspruch 11, dadurch gekennzeichnet, daß das Pulver in einer Menge von 40 - 99,9 %, bezogen auf die Gesamtmasse des Keramikbindemittels und des Pulvers, verwendet wird.
13. Formteil gemäß Anspruch 7, dadurch gekennzeichnet, daß das Verstärkungsmaterial aus Fasern besteht, die in dem Formteil dispergiert sind, wobei das Keramikmaterial als Grundmasse dient.
14. Formteil gemäß Anspruch 13, dadurch gekennzeichnet, daß die Fasern in einer Menge von 5 - 75 Vol.-% verwendet werden.
15. Formteil gemäß Anspruch 7, dadurch gekennzeichnet, daß das Verstärkungsmaterial eine Mischung aus Fasern und Pulver ist, wobei die Fasern in dem Formte dispergiert sind, dabei das Keramikmaterial als Grundmasse dient und das Pulver in dieser Keramikgrundmasse dispergiert ist.
16. Formteil gemäß Anspruch 15, dadurch gekennzeichnet, daß die Fasern in einer Menge von 5 - 75 Vol.-% verwendet werden.
17. Formte gemäß Anspruch 15 oder 16, dadurch gekennzeichnet, daß das Pulver in einer Menge von 0,1 - 60 %, bezogen auf die Gesamtmasse der Keramikgrundmasse und des Pulvers, verwendet wird.
18. Verfahren zur Herstellung eines Formteils, wie es in einem der vorhergehenden Ansprüche definiert ist, wobei das Verfahren aus folgenden Schritten besteht:
 Füllen eines Formhohlraumes mit einem das Polysilazan enthaltenden Ausgangsmaterial;
 Erhitzen des Ausgangsmaterials von Raum-

température auf etwa 400 °C, so daß das Polysilazan im Formhohlraum fest wird; und

Kalzinieren des festgewordenen Produkts zu einem Formartikel aus dem Keramikmaterial auf Siliciumnitridbasis durch Erhitzen auf 500 - 1 700 °C mit einer Erhitzungsgeschwindigkeit bis zu 20 °C/min.

19. Verfahren gemäß Anspruch 18, dadurch gekennzeichnet, daß das Ausgangsmaterial des weiteren ein Keramikpulver enthält, so daß das Keramikpulver in einer Grundmasse des Keramikmaterials auf Siliciumnitridbasis dispergiert ist.

20. Verfahren gemäß Anspruch 19, dadurch gekennzeichnet, daß das Keramikpulver aus einem Metallnitrid, -carbid oder -oxid besteht.

21. Verfahren zur Herstellung eines Formteils, wie es in einem der Ansprüche 1 - 7 definiert ist, wobei das Verfahren folgende Schritte umfaßt:

Imprägnieren der Fasern mit einer das Polysilazan enthaltenden Flüssigkeit;

Festwerdenlassen des Polysilazans zu einem Prepreg; und

Kalzinieren und Sintern des so gebildeten Prepregs bei einer Temperatur von 700 - 2 500 °C mit einer Erhitzungsgeschwindigkeit bis zu 20 °C/min zu einer faserverstärkten Keramikmasse auf Siliciumnitridbasis.

22. Verfahren gemäß Anspruch 21, dadurch gekennzeichnet, daß die Flüssigkeit des weiteren ein darin dispergiertes feines Keramikpulver enthält.

23. Verfahren zur Herstellung eines Formteils, wie es in einem der Ansprüche 1 - 17 definiert ist, wobei das Verfahren folgende Schritte umfaßt:

Herstellen einer Lösung des Polysilazans;
Mischen der Lösung mit einem feinen Keramikpulver zu einer Schlamm;

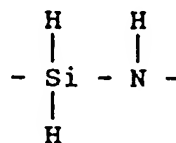
Formen der Schlamm zu einem Formteil, wobei das Polysilazan als Bindemittel dient; und

Kalzinieren des Formteils bei einer Temperatur von 600 - 2 300 °C zu einem Keramikformartikel auf Siliciumnitridbasis.

Revendications

1. Corps façonné contenant une céramique à base de nitrure de silicium, contenant Si et N en quantités procurant un rapport atomique N/Si de 0,04 à 3, et au moins un métal choisi dans les groupes IIA, III, IV et V de la classification périodique, en quantité procurant un rapport atomique M/Si de 9 ou moins, où M désigne ledit ou lesdits métaux des groupes IIA, III, IV et V, et éventuellement de l'oxygène en une quantité procurant un rapport atomique O/Si de 0,05-15, dans lequel ladite céramique est obtenue

à partir d'un polymétallosilazane possédant un rapport atomique métal/silicium de 0,001-30 et une masse moléculaire en nombre de 200-500 000, que l'on obtient en faisant réagir une matière première ayant une masse moléculaire de 100-50 000 et le motif récurrent suivant:



avec un alcoxyde métallique de formule $\text{M}(\text{OR})_n$, dans lequel M est un métal du groupe IIA, III, IV ou V de la classification périodique, R_4 est un atome d'hydrogène, un groupe alkyle comportant 1-20 atomes de carbone ou un groupe aryle, et n est la valence du métal M, à condition qu'au moins un substituant R_4 soit un groupe alkyle ou aryle; et dans lequel la teneur en carbone de la céramique est telle que le rapport atomique C/Si soit de 0,66 ou moins.

2. Corps façonné selon la revendication 1, dans lequel lesdits rapports atomiques sont les suivants:

N/Si:	0,1-1,7, et
M/Si:	5 ou moins, et, le cas échéant,
O/Si:	0,1-10.

3. Corps façonné selon la revendication 2, dans lequel lesdits rapports atomiques sont les suivants:

N/Si:	0,3-1,3, et
M/Si:	2,5 ou moins, et, le cas échéant,
O/Si:	0,3-4.

4. Corps façonné selon l'une quelconque des revendications précédentes et ayant une résistance au pliage en trois points de 20 kg/cm² ou plus.

5. Corps façonné selon l'une quelconque des revendications précédentes, dans lequel ladite céramique contient de fins cristallites de céramique, ayant un diamètre de 2 000 Å ou moins.

6. Corps façonné selon l'une quelconque des revendications 1-4, dans lequel ladite céramique est de nature essentiellement amorphe.
7. Corps façonné selon l'une quelconque des revendications précédentes, contenant, en outre, un matériau de renfort. 5
8. Corps façonné selon la revendication 7, dans lequel ledit matériau de renfort est sous forme de poudre et est dispersé de façon homogène dans ledit corps moulé, ladite céramique servant de matrice. 10
9. Corps façonné selon la revendication 8, dans lequel ladite poudre est utilisée en une quantité de 0,1-60% par rapport au poids total de ladite matrice de céramique et de ladite poudre. 15
10. Corps façonné selon la revendication 8 ou la revendication 9, dans lequel ledit matériau de renfort est une poudre de céramique. 20
11. Corps façonné selon la revendication 7, dans lequel ledit matériau de renfort est sous la forme d'une poudre liée avec ladite céramique, qui sert de liant. 25
12. Corps façonné selon la revendication 11, dans lequel ladite poudre est employée dans une proportion de 40-99,9% par rapport au poids total dudit liant céramique et de ladite poudre. 30
13. Corps façonné selon la revendication 7, dans lequel ledit matériau de renfort est sous la forme de fibres dispersées dans ledit corps façonné, ladite céramique servant de matrice. 35
14. Corps façonné selon la revendication 13, dans lequel lesdites fibres sont employées dans une proportion de 5-75% en volume. 40
15. Corps façonné selon la revendication 7, dans lequel ledit matériau de renfort est un mélange de fibres et de poudre, lesdites fibres étant dispersées dans ledit corps façonné, ladite céramique servant de matrice, et ladite poudre étant dispersée dans ladite matrice de céramique. 45
16. Corps façonné selon la revendication 15, dans lequel lesdites fibres sont employées dans une proportion de 5-75% en volume. 50
17. Corps façonné selon la revendication 15 ou la revendication 16, dans lequel ladite poudre est employée dans une proportion de 0,1-60% par rapport au poids total de ladite matrice de céramique et de ladite poudre. 55
18. Procédé de production d'un corps façonné tel que défini dans l'une quelconque des revendications précédentes, comprenant les étapes qui consistent à:
 - remplir une empreinte de moule avec une matière première contenant ledit polysilazane;
 - chauffer ladite matière première à une température allant de la température ambiante à environ 400°C pour solidifier ledit polysilazane dans ladite empreinte de moule; et
 - calciner ledit produit solidifié pour obtenir un article moulé, formé de ladite céramique à base de nitrure de silicium, en chauffant ledit produit solidifié à 500°-1 700°C à une vitesse de montée en température de 20°C/min ou moins.
19. Procédé selon la revendication 18, dans lequel ladite matière première contient aussi une poudre de céramique, de manière à ce que ladite poudre de céramique soit dispersée dans une matrice de ladite céramique à base de nitrure de silicium.
20. Procédé selon la revendication 19, dans lequel ladite poudre de céramique est formée d'un nitrure métallique, d'un carbure métallique ou d'un oxyde métallique.
21. Procédé de production d'un corps façonné tel que défini dans l'une quelconque des revendications 1-7, comprenant les étapes qui consistent à:
 - imprégner les fibres avec un liquide contenant ledit polysilazane;
 - solidifier ledit polysilazane pour former un préimprégné; et
 - calciner et fritter le préimprégné ainsi formé à une température de 700°-2 500°C, avec une vitesse de montée en température de 20°C/min ou moins, pour former un corps céramique à base de nitrure de silicium renforcé par des fibres.
22. Procédé selon la revendication 21, dans lequel ledit liquide contient aussi de la poudre de céramique finement divisée, dispersée dans ce liquide.
23. Procédé de production d'un corps façonné tel que défini dans l'une quelconque des revendications 1-17, comprenant les étapes qui consistent à:
 - obtenir une solution dudit polysilazane;
 - mélanger ladite solution avec une poudre de céramique finement divisée pour former une suspension;
 - mouler ladite suspension pour former un corps moulé, ledit polysilazane servant de liant; et
 - calciner ledit corps moulé à une température de 600°-2 300°C pour former un article moulé en céramique, à base de nitrure de silicium.